



United States  
Environmental Protection  
Agency

# Envirogen Propane Biostimulation Technology for In-Situ Treatment of MTBE- Contaminated Ground Water

## Innovative Technology Evaluation Report



# **Envirogen Propane Biostimulation Technology for In-Situ Treatment of MTBE-Contaminated Ground Water**

## **Innovative Technology Evaluation Report**

Prepared by:

Technical Project Manager

Ann Azadpour-Keeley  
Subsurface Protection and Remediation Division  
National Risk Management Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Ada, OK 74820

National Risk Management Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Cincinnati, Ohio 45268

## **NOTICE**

The U.S. Environmental Protection Agency (EPA) through its Office of Research and Development funded the information described here by Ann Keeley, the EPA TPM and WAM for this demonstration, under contract 68-C-98-138 to ManTech Environmental Research Services Corp. and 68-C-00-179 to SAIC. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute an endorsement or recommendation for use.

All research projects making conclusions or recommendations based on environmental data funded by the U.S. Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project was conducted under an approved Quality Assurance Project Plan. The procedures specified in this plan were used without exception. Information on the plan and documentation of the quality assurance activities and results are available from the principal Investigator.

## FOREWORD

The U.S. Environmental Agency (EPA) is charged by Congress with protecting the nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and ground water; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

The purpose of this publication is to present information that will assist decision-makers in evaluating an innovative remedial technology for application to cleanup of sites with contaminated ground water. This ITER, which has been produced as part of the Laboratory's strategic long-term research plan, describes the effectiveness and applicability of the propane biostimulation technology developed by Envirogen as a potential in-situ remedial alternative for the mineralization of MTBE from contaminated ground water. This technology was demonstrated and evaluated at the Naval Base Ventura County at Port Hueneme, California. Spatial and temporal data to evaluate the technology were collected from a dense network of in-situ monitoring points over a period in excess of 300 days. This comprehensive evaluation of the Envirogen technology demonstrated that its application at this site did not meet the State of California's treatability criteria.

Stephen G. Schmelling, Acting Director  
Subsurface Protection and Remediation Division  
National Risk Management Research Laboratory

## **ABSTRACT**

The primary objective of the Biostimulation Technology Evaluation was to determine if enhanced biodegradation was occurring in a ground-water Test Plot to a sufficient degree to reduce intrinsic methyl tertiary butyl ether (MTBE) to the State of California's treatability criteria of 5 µg/L or below. The project was carried out at the National Environmental Technology Test Site (NETTS) at the (NBVC) Naval Base Ventura County, Port Hueneme, California where a hydrocarbon release into ground water occurred between September 1984 and March 1985 involving approximately 4,000 gallons of leaded and 6,800 gallons of unleaded premium gasoline.

The geology at the site consists of unconsolidated sediments composed of sands, silts, clays and minor amounts of gravel and fill material. A shallow, perched, unconfined aquifer is the uppermost water-bearing unit. The water table is generally encountered at depths between 6 to 8 feet below ground surface (BGS), and has a saturated aquifer thickness of 16 to 18 feet.

The evaluation was carried out between June 2001 and March 2002 using Control and Test Plots and a cadre of primary and secondary analytes through 15 sampling events. The goals of the project were approached with the use of deuterated MTBE (d-MTBE) and ground-water tracers including bromide and iodide.

An analysis of intrinsic MTBE, deuterated MTBE, daughter products, and geochemical parameters demonstrated that the technology did not meet the State of California's treatability criteria.

## TABLE OF CONTENTS

<b><u>Section</u></b>	<b><u>Page</u></b>
NOTICE.....	ii
FOREWORD.....	iii
ABSTRACT.....	iv
LIST OF FIGURES.....	viii
LIST OF TABLES.....	ix
ACRONYMS, ABBREVIATIONS, AND SYMBOLS.....	x
ACKNOWLEDGEMENTS.....	xiii
 EXECUTIVE SUMMARY.....	 1
 SECTION 1 INTRODUCTION.....	 5
1.1 PURPOSE AND ORGANIZATION OF THE ITER.....	5
1.2 DESCRIPTION OF THE MTBE DEMONSTRATION PROGRAM.....	6
1.3 TECHNOLOGY DESCRIPTION.....	7
1.3.1 Principles of the Propane Biostimulation Technology.....	7
1.3.2 Demonstration System Design.....	11
1.4 KEY CONTACTS.....	13
 SECTION 2 DEMONSTRATION OBJECTIVE AND EVALUATION JUSTIFICATION.....	 15
2.1 BACKGROUND.....	15
2.1.1 NBVC Site Characterization.....	16
2.1.2 Site Description.....	16
2.1.3 Hydrogeology.....	16
2.1.4 Contaminant Distribution.....	17
2.2 TECHNOLOGY DEMONSTRATION SITE PRE-CHARACTERIZATION.....	17
2.3 DEMONSTRATION OBJECTIVE.....	19
2.3.1 Primary Objective – A Critical Measurement.....	21
2.3.2 Secondary Objectives – Non-Critical Measurements.....	22
2.4 SCHEDULE.....	28
 SECTION 3 PERFORMANCE MONITORING APPROACH.....	 30
3.1 TRACER STUDY COMPOUNDS.....	30
3.1.1 Test and Control Design.....	35
3.1.2 Monitoring Parameters.....	36
3.1.3 Sampling Approach.....	36
 SECTION 4 SAMPLING AND ANALYSIS PROTOCOL.....	 38
4.1 GROUND-WATER SAMPLING.....	38
4.1.1 Monitoring Well Specifications.....	38
4.1.2 Low Flow Sampling.....	38

## TABLES OF CONTENTS (Continued)

4.1.3	Well Purging.....	39
4.1.4	Well Sampling .....	39
4.2	TRACER INJECTION SYSTEM OPERATION AND MAINTENANCE.....	41
SECTION 5	PRE-DEMONSTRATION INVESTIGATION.....	45
5.1	BROMIDE TRACER TEST .....	45
SECTION 6	TREATMENT EFFECTIVENESS - RESULTS .....	49
6.1	DEMONSTRATION OBJECTIVES AND APPROACH .....	49
6.2	DEMONSTRATION PROCEDURES.....	49
6.2.1	MTBE Reduction .....	50
6.2.2	d-MTBE Reduction .....	54
6.2.3	Daughter Products .....	59
6.2.4	Water Quality Measurements.....	62
6.3	WATER LEVEL MEASUREMENTS.....	64
SECTION 7	TREATMENT EFFECTIVENESS – CONCLUSIONS.....	71
7.1	BACKGROUND.....	71
7.2	PERFORMANCE ANALYSIS .....	72
7.2.1	Qualified Monitoring Points.....	73
7.2.2	Statistical Analysis of Results .....	74
7.3	EVALUATION OF RESULTS AGAINST OBJECTIVE.....	85
7.4	QUALITY ASSURANCE AND QUALITY CONTROL RESULTS .....	89
SECTION 8	ECONOMIC ANALYSIS .....	94
8.1	INTRODUCTION.....	94
8.2	APPLICATION ISSUES AND ASSUMPTIONS.....	95
8.2.1	Site-Specific Factors .....	97
8.2.2	Equipment and Operating Parameters .....	97
8.2.3	Base-Case Scenario .....	99
8.3	COST CATEGORIES .....	100
8.3.1	Site Preparation Costs .....	100
8.3.2	Permitting and Regulatory Costs.....	101
8.3.3	Mobilization and Startup Costs .....	102
8.3.4	Equipment Costs.....	103
8.3.5	Labor Costs .....	103
8.3.6	Supply Costs.....	104
8.3.7	Utility Costs.....	104
8.3.8	Effluent Treatment and Disposal Costs.....	105
8.3.9	Residual Waste Shipping and Handling Costs .....	105
8.3.10	Analytical Services Costs.....	105
8.3.11	Equipment Maintenance Costs.....	106
8.3.12	Site Demobilization Costs .....	106

## TABLES OF CONTENTS (Continued)

8.4	CONCLUSIONS OF ECONOMIC ANALYSIS .....	106
SECTION 9	TECHNOLOGY APPLICATIONS ANALYSIS .....	108
9.1	TECHNOLOGY PERFORMANCE VERSUS ARARS .....	108
9.2	TECHNOLOGY OPERABILITY .....	109
9.3	KEY FEATURES OF THE TREATMENT TECHNOLOGY .....	110
9.4	APPLICABLE WASTES .....	110
9.5	AVAILABILITY AND TRANSPORTABILITY OF EQUIPMENT .....	111
9.6	MATERIALS HANDLING REQUIREMENTS.....	111
9.7	RANGE OF SUITABLE SITE CHARACTERISTICS .....	111
9.7.1	Site Support Requirements .....	112
9.8	LIMITATIONS OF THE TECHNOLOGY .....	112
9.9	POTENTIAL REGULATORY REQUIREMENTS .....	113
SECTION 10	TECHNOLOGY STATUS .....	119
10.1	PREVIOUS EXPERIENCE .....	119
10.2	SCALING CAPABILITIES .....	120
REFERENCES	.....	121
APPENDIX A	VENDOR’S CLAIMS .....	A-1



## List of Figures

<u>Number</u>		<u>Page</u>
1-1	Port Hueneme Plume Map .....	8
1-2	Site Location.....	9
1-3	In-Situ Application of Propane Biostimulation.....	10
1-4	Piping and Instrumentation Diagram.....	14
3-1	Test and Control Plots Layout.....	32
3-2	Tracer Circulation Well.....	33
3-3	Tracer Circulation System Cross Section.....	34
3-4	Well Construction Specifications.....	37
6-1	MTBE Concentration in the Vicinity of the Envirogen Site on October 4, 2000.....	50
6-2	MTBE Concentration in the Vicinity of the Envirogen Site on November 11, 2000 .....	51
6-3	The Average Deep Screen MTBE Concentrations in the Test and Control Plots .....	52
6-4	MTBE by Flow Paths (Columns) in Test Plot .....	53
6-5	MTBE by Flow Paths (Columns) in Control Plot .....	54
6-6	d-MTBE in Downgradient Columns of Test Plot.....	56
6-7	d-MTBE in Downgradient Columns of Control Plot .....	56
6-8	Downgradient d-MTBE Concentration in Control and Test Plots.....	59
6-9	Static Water Levels in Test Plot.....	66
6-10	Maximum Water Levels in Test Plot .....	67
6-11	Static Water Levels in Control Plot.....	68
6-12	Maximum Water Levels in Control Plot .....	69
6-13	Pictures of Water Spouts at the Surface Through Monitoring Wells.....	70
7-1	Test Plot Normal Distribution .....	79
7-2	Control Plot Normal Distribution.....	80
7-3	Probability Plot MTBE in Test Plot .....	81
7-4	Probability Plot MTBE in Control Plot.....	82
7-5	MTBE Time Trends for Test and Control Plots.....	83
7-6	Time Trends of Total d-MTBE Mass in Test and Control Plots.....	84
7-7	Downgradient Test Plot MTBE Concentrations at the Bottom Screens .....	86

## List of Tables

<u>Number</u>		<u>Page</u>
2-1	Summary of Site Characterization Analytical Results for Contaminants of Concern at the Middle Zone .....	25
2-2	Analyses to Support the Propane Biostimulation and Bioaugmentation Project Objectives .....	26
2-3	Applicable Regulatory Criteria for MTBE Treatment Technology Demonstration Program.....	27
2-4	U.S. EPA Performance Monitoring Sampling Schedule.....	29
4-1	Analytical Parameters and Method Requirements .....	44
5-1	Initial Breakthrough Periods for Downgradient Observation Points .....	47
6-1	Detection of d-MTBE in Upgradient Monitoring Wells.....	58
6-2	Daughter Products in Control Plot .....	61
6-3	Daughter Products in Test Plot.....	61
6-4	Water Quality Measurements in Control Plot.....	63
6-5	Water Quality Measurements in Test Plot .....	63
7-1	Qualified Monitoring Wells .....	75
8-1	Estimated Cost for Envirogen Propane Biostimulation and Bioaugmentation Project at a Typical Gas Station .....	96

## ACRONYMS, ABBREVIATIONS, AND SYMBOLS

ALSI	Analytical Laboratory Services, Inc.
ARAR	Applicable or relevant and appropriate requirement
BIPT	Bacterial injection point in the Test Plot
Br <sup>-</sup>	Bromide ion
BGS	Below ground surface
BTEX	Benzene, toluene, ethylbenzene, and xylenes
CAA	Clean Air Act
CERCLA	Comprehensive Emergency Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CFU	Colony Forming Units
Cl <sup>-</sup>	Chloride ion
CO <sub>2</sub>	Carbon dioxide
COC	Chain-of-Custody
CPT	Cone Penetrometer Technology
CWA	Clean Water Act
DBPR	Disinfection By-Product Rule
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DOE	Department of Energy
d-MTBE	Deuterated methyl tert-butyl ether
EPA	U.S. Environmental Protection Agency
ITER	Innovative Technology Evaluation Report
LCS/LCSD	Laboratory control samples and laboratory control sample duplicates
MCL/MCLG	Maximum Contaminant Level and Maximum Contaminant Level Goal
MDL	Method detection limit
µg/L	Microgram per liter
mg/L	Milligram per liter
MS/MSD	Matrix spike/matrix spike duplicate
MTBE	Methyl tert-butyl ether
NAAQS	National Ambient Air Quality Standard
NETTS	Department of Defense National Environmental Technology Test Site

## ACRONYMS, ABBREVIATIONS, AND SYMBOLS (Continued)

NBVC	Naval Base Ventura County
NEX	Naval Exchange
NFESC	Naval Facilities Engineering Service Center
NRMRL	National Risk Management Research Laboratory
OIPC	Oxygen injection point in the Control Plot
OIPT	Oxygen injection point in the Test Plot
OSWER	Office of Solid Waste and Emergency Response
PIPT	Propane injection point in the Test Plot
PMO	Propane monooxygenase
POB	Propane oxidizing bacteria
ppm	Part per million
PQA	Pre-Quality Assurance Project Plan Agreement
QA	Quality assurance
QAPP	Quality assurance project plan
QC	Quality control
RCRA	Resource Conservation and Recovery Act
RRF	Relative response factor
RPD	Relative percent difference
SAIC	Science Applications International Corporation
SDWA	Safe Drinking Water Act
SPRD	Subsurface Protection and Remediation Division
STDEV	Standard Deviation
SVE	Soil vacuum extraction
SVOC	Semi-volatile organic compound
TBA	<i>tert</i> -butyl alcohol
TCE	Trichloroethene
TPM	Technical Project Manager
TOC	Total organic carbon
TSCA	Toxic Substance Control Act
TSA	Technical system audit

## **ACRONYMS, ABBREVIATIONS, AND SYMBOLS (Continued)**

UCL	Upper confidence limit
VMP	Vapor monitoring point
VOA	Volatile organic analysis
VOC	Volatile organic compound
WAM	Work Assignment Manager
WQCB	Water Quality Control Board
WQS	Water quality standard

## ACKNOWLEDGMENTS

This report was prepared for the U.S. Environmental Protection Agency (EPA) by Ann Keeley, the EPA Technical Project Manager and Work Assignment Manager for this demonstration, at the National Risk Management Research Laboratory (NRMRL) in Ada, Oklahoma. The technology evaluation process was a cooperative effort that involved personnel from the EPA Office of Research and Development (ORD), EPA Region 9, U.S. Navy, California Water Quality Control Board (WQCB), and Envirogen.

The extensive effort of the following personnel during this project is gratefully acknowledged:

- Fran Kremer, Annette Gatchett, Bob Olexsey, and Steve Schmelling of NRMRL and Arlene Kabei of Region 9 for the composition of an outstanding management team for the overall MTBE demonstration evaluation program;
- The NRMRL QA Managers Ann Vega and Steve Vandegrift for their crucial roles in association with the various aspects of the quality assurance and quality control of this demonstration;
- Drs. Carl Enfield, John Wilson, and Randall Ross for their technical advice;
- Peter Raftery as well as the WQCB management for their technical and administrative efforts in granting the project permits;
- ManTech, a SPRD contractor for performing various tasks including system installation, sampling execution, and laboratory analytical services; and
- SAIC, a NRMRL contractor for the development of the project QAPP.

Special thanks are offered to the employees at the U.S. Navy, Naval Facilities Engineering Service Center (NFESC) host site for their hospitality and assistance throughout this demonstration, especially, Ernie Lory, Dorothy Cannon, and James Osgood.